Production of dimethyl-2,6-naphthalenedicarboxylate: precursor to polyethylene naphthalate

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Abstract

The development of the commercialization of 2,6-naphthalenedicarboxylic acid (2,6-NDA), dimethyl-2,6-naphthalenedicarboxylate (2,6-NDC) and their homopolymer with ethylene glycol, polyethylene naphthalate (PEN), is reviewed. Many of the significant alternative chemical routes to produce 2,6-dimethylnaphthalene (2,6-DMN), the main precursor to 2,6-NDA, are discussed and evaluated. The *o*-xylene + butadiene multi-step route of BP Amoco's first-in-the-world large scale commercial plant built in Decatur, Alabama is described. Production economics of some of the major 2,6-NDC precursors are described. Physical properties of the 2,6-DMN intermediates, 2,6-NDA and 2,6-NDC, are given along with some discussion on the methods of purification of the dibasic naphthalate monomers. Polymer applications for PEN and manufacturing economics of PEN versus PET are compared, and finally, engineering resins incorporating 2,6-NDA and 2,6-NDC are described. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 2,6-Dimethylnaphthalene (2,6-DMN); Polyethylene naphthalate (PEN); Dimethyl-2,6-naphthalenedicarboxylate (2,6-NDC); 2,6-Naphthalenedicarboxylic acid (2,6-NDA)

1. Introduction and background

2,6-Naphthalenedicarboxylic acid (2,6-NDA) and its dimethyl ester (2,6-NDC) have been long sought after as the feedstock(s) for the high performance polyester polyethylene naphthalate (PEN, Fig. 1a).

2,6-NDA had been of casual interest since the late 1950s when terephthalic acid and dimethyl terephthalate were beginning to exhibit exciting growth potential as feedstocks for polyethylene terephthalate (PET). BP Amoco investigated the production of 2,6-NDA and 2,6-NDC (Fig. 1b (1) and (2)) as early as 1958, and later produced developmental quantities by oxidation of 2,6-dimethylnaphthalene (DMN) isolated from heavy ultraformer bottoms during 1973–1975 (Fig. 1b).

The metal-catalyzed process for liquid phase oxidation of alkylated aromatic hydrocarbons was originally discovered by Scientific Design Company (Mid-Century Oxidation (MC Oxidation)) in 1953 [1], and was purchased by BP Amoco in 1956. The first commercial unit was constructed by BP Amoco in 1958 at its Joliet, Illinois facility for the manufacture of mixed benzene mono- and di-carboxylic acids. Further process development and a market interest led to specialized continuous oxidation plants for the manufacture of terephthalic acid and isophthalic acid.

Teijin introduced semi-commercial quantities of an improved polyester, PEN, into the market place in the early 1970s. Introduced as an extruded film tradenamed "Q-polymer", it featured higher modulus,

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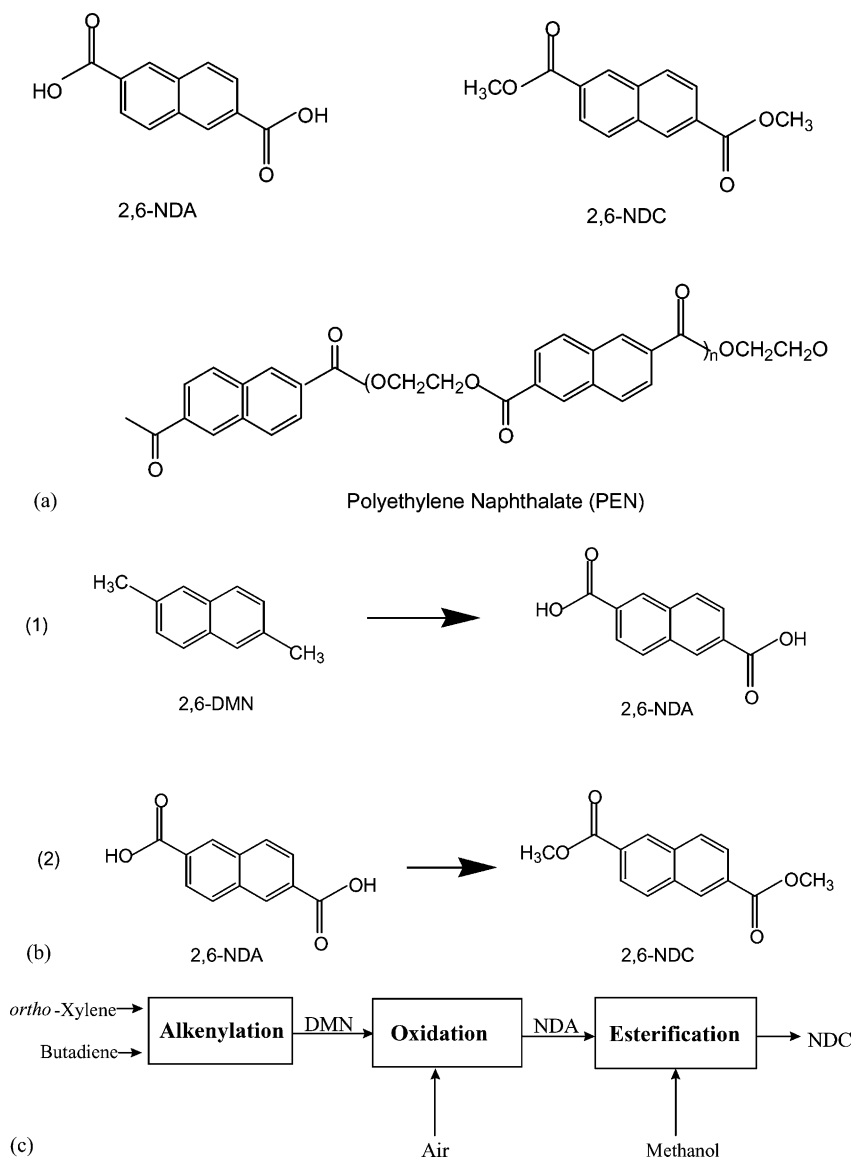*E-mail address:* lillwitzathome@aol.com (L.D. Lillwitz).

Fig. 1. (a) Scheme of PEN; (b) production of 2,6-NDA and 2,6-NDC; (c) BP Amoco 2,6-NDC process block diagram.

outstanding heat resistance and improved dimensional stability. It also had mechanical, chemical and electrical properties superior to PET film. This material quickly found use in audio and video tape applications in place of the conventional PET film. Several companies expressed an interest in PEN applications. The 3M company was interested in using PEN film for magnetic recording tape for computers and Goodyear

was interested in using PEN fiber for belts in radial tires. Other companies were interested in its use in electrical insulation applications.

Market estimates showed the demand for PEN growing to 10–15 million lb per year by 1980. With this type of anticipated growth, a commercial, economical process had to be found to produce the naphthalenedicarboxylate feedstock in sufficient quantities.
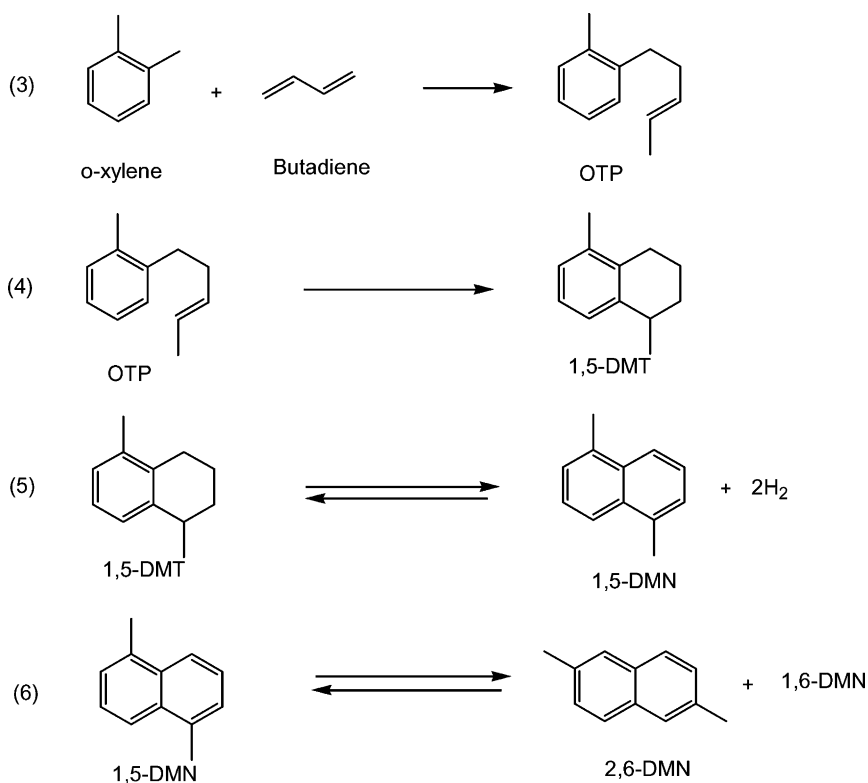
Scheme 1.

Sun Oil and Teijin were two other companies besides BP Amoco that were highly interested and active in the late 1960s and early 1970s in research efforts to develop a process to produce 2,6-NDA. One of their efforts was a non-synthetic approach based on the isolation of monomethyl naphthalenes from feedstock employed for naphthalene manufacture [2–4]. However, the failing with using this feedstock was the assurance of adequate availability. Another approach they looked at was a synthetic route to 2,6-DMN via an o-xylene + butadiene condensation [5–10] as shown in Scheme 1.

Eventually a cooperative research program was established between Sun Oil and Teijin to select and develop the best technology for commercial manufacture of 2,6-DMN (the best feedstock for oxidation to 2,6-NDA). Earlier, Teijin had worked on another isolation route and they showed that DMN could be isolated from refinery streams and oxidized to 2,6-NDA. To accomplish the isolation they developed

a process based on a clathration of 2,6-DMN with m-nitro benzoic acid from light catalytic gas oil (LCGO). But even though this route had encouraging economics, it was eliminated early in this program because of insufficient LCGO or other 2,6-DMN containing streams in one refinery location to feed a plant of sufficient size to supply the projected growing market. Shortly thereafter the decision was made to develop the o-xylene + butadiene route, and a complete process design was produced. However, commercialization of this synthetic route to 2,6-NDA through 2,6-DMN was abandoned when the market for PEN failed to materialize as expected.

By 1984, there was sufficient market interest to encourage BP Amoco to begin regular production of developmental quantities of 2,6-NDA. During the period 1985–1993 BP Amoco produced several million pounds of 2,6-NDA, and most of it was converted to the dimethyl ester. During this same time period, Eastman Chemical was developing PEN for container

applications, because of PEN's high temperature properties and its five-fold increased oxygen barrier compared to PET. This development once again fueled the market interest in 2,6-NDA.

By the mid 1980s, BP Amoco also abandoned its efforts to isolate 2,6-DMN from refinery streams because of availability and poor economics. After careful review of the potential routes to 2,6-NDA, they decided the *o*-xylene + butadiene route (Scheme 1) offered the best combination of technical feasibility and economics. A BP Amoco team was formed to develop and commercialize this technology, with the Sun–Teijin chemistry used as the starting point for BP Amoco's development of its 2,6-DMN process. Each of the four steps shown in Scheme 1 (3–6) were carefully investigated in addition to the oxidation and esterification steps (1–2).

Also, in the early 1990s, two Japanese groups, Mitsubishi Gas Chemical (MGC) and Nippon Steel/Chiyoda became active in the chase to commercialize 2,6-NDA. MGC developed a process based on the selective acylation of 2-methylnaphthalene [acyl methylnaphthalene (AMN) or 2-methyl-6-isobutyrylnaphthalene (MIBN)], and Nippon Steel/Chiyoda's process was based on isopropylation of naphthalene to give 2,6-di-isopropyl naphthalene (DIPN) [11,12]. In both these processes, the above intermediates were oxidized to 2,6-NDA. Also, both processes were built on the semi-commercial scale of about 1–2 million lb. Actually, during this period, Nippon Steel had three different technologies that they were simultaneously involved in developing: (1) the DIPN process; (2) a diethylnaphthalene (DEN) process; (3) and a modified Henkel process.

Since the early 1990s, MGC has investigated several other 2,6-NDA processes. They had intended to commercialize a unit based on the *o*-xylene + butadiene chemistry at the 44 million lb per year scale [13], but eventually the size of the unit was kept to the commercial development scale of 1–2 million lb per year.

During the development phase of the BP Amoco *o*-xylene + butadiene, 2,6-NDC process, BP Amoco performed many technical and economic reviews of alternative technologies. In addition to the processes mentioned above, two other significant examples that were evaluated were carbonylation technologies (see Sections 2.1 and 2.3). Each of these reviews increased BP Amoco's confidence that it had chosen to develop

the most technically feasible and economic process. The first world scale 2,6-NDC plant (60 million lb per year capacity) started up at BP Amoco's Decatur, Alabama site in 1995.

2. Competitive chemistries to NDC/NDA

Since the late 1950s, when commercial interest in the production of 2,6-NDA became apparent, many companies have studied a wide range of refinery stream isolation and synthetic schemes aimed at its economical production. In the following section, some of the major routes that have been studied and proposed in various reports are discussed, yet they have not been commercialized in significant scale to date for technical or economic reasons.

2.1. Di-iodonaphthalene carbonylation

In the 1980s, Eastman Chemical developed the two-step process shown in Scheme 2 that avoided the alkyl aromatic oxidation step (MC oxidation), and focused on their carbonylation technology. The first step involves the oxyiodination of naphthalene over a solid catalyst containing alkali or alkaline earth cations [14]. A later report describes the oxyiodination over basic faujasite zeolites (KX) [15]. The carbonylation step most probably involves a homogeneous rhodium catalyst reacted in the presence of water to produce the dicarboxylic acid, or reacted in the presence of methanol to produce the dicarboxylic ester [16,17] (Scheme 2).

The negative aspects of this process are high costs and containment of the rhodium and iodine, the corrosiveness and environmental issues of the iodine systems, the low conversions of the individual steps, the lack of selectivity of the iodination reaction and the complex separation of the iodo isomers.

2.2. Modified Henkel (transcarboxylation)

Nippon Steel was very active in the area of aromatics isolation from coal tar distillates. An early route they looked at was the isolation of acenaphene, oxidation to 1,8-NDA and then isomerization to 2,6-NDA (Henkel reaction). Later, using their experience in Henkel chemistry, they developed the process shown
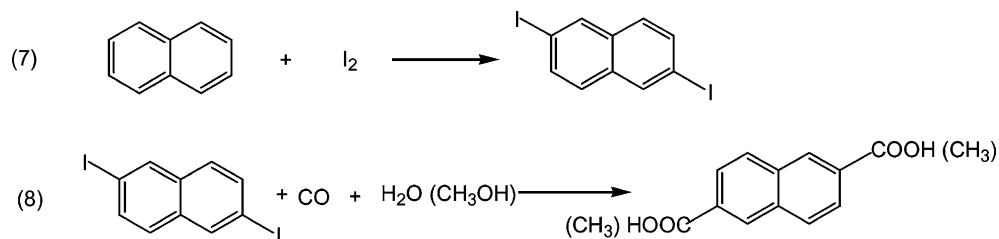
Scheme 2.

in Scheme 3, which is based on the transcarboxy-lation of naphthalene with the dipotassium salt of phthalic acid using a cadmium iodine-cesium iodide catalyst system [18]. These processes rely very heavily on solids handling, and are therefore very difficult processes to develop.

2.3. Alkyl aromatic acylation

MGC has explored many potential routes to 2,6-NDA. As mentioned earlier, they first proposed a process based on the acylation of 2-methylnaphthalene. Initially they explored a process based on acylation with acetyl fluoride to produce 2-methyl-6-acylnaphthalene (2,6-AMN) [19]. Later their efforts shifted to hydrogen fluoride-boron trifluoride-catalyzed acylation with propylene + carbon monoxide to produce 2-methyl-6-isobutyrylnaphthalene (2,6-MIBN) [20–23]. The 2-methyl-6-acylnaphthalene was then oxidized in a second step to 2,6-NDA [24]. This route is shown in Scheme 4.

This process went through the early stages of development, but was dropped in favor of two additional routes which also feature hydrogen fluoride-boron trifluoride catalysis, one of MGC's core catalyst technologies [25]. The more favored of these two new processes uses toluene, butene and carbon monoxide as the key feedstocks [26] and is shown in Scheme 5.

The carbonylation step in this multi-step process produces a dialkyl benzene (p-tolyl-sec-butylketone) similar to 5-(o-tolyl)-pentene-2 (5-OTP) produced in the o-xylene + butadiene route. This is followed by hydrogenation, dehydration and dehydrocyclization to produce 2,6-DMN. No isomerization step is required, because the dehydrocyclization gives the 2,6 isomer selectively. The overall yield is 66% (Scheme 5).

The other route is very similar to the above route, but it is based on m-xylene, propylene, and carbon monoxide [27]. The sequence and number of reaction steps is the same as the above route. This process, shown in Scheme 6, is lower yielding however (55%), because the dehydro-cyclization reaction is more difficult and less selective.

The catalysts used for the parallel reactions in each of these two processes are very similar. Following the hydrogen fluoride-boron trifluoride-catalyzed carbonylation, the hydrogenation and dehydration are carried over traditional copper chromite and alumina catalysts, respectively. The cyclodehydration reaction catalysts are 10% copper oxide for the toluene route and 5% potassium oxide on alumina for the m-xylene route.

BP Amoco carefully evaluated these two processes, and compared them to the o-xylene + butadiene process they were developing. The major disadvantages of these processes are the low overall process yields
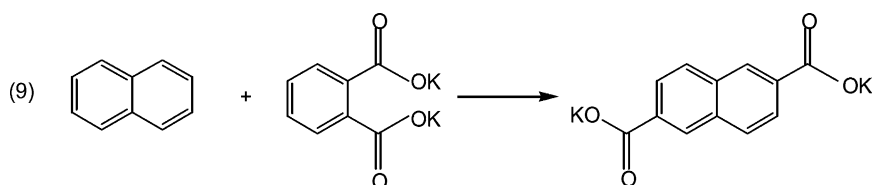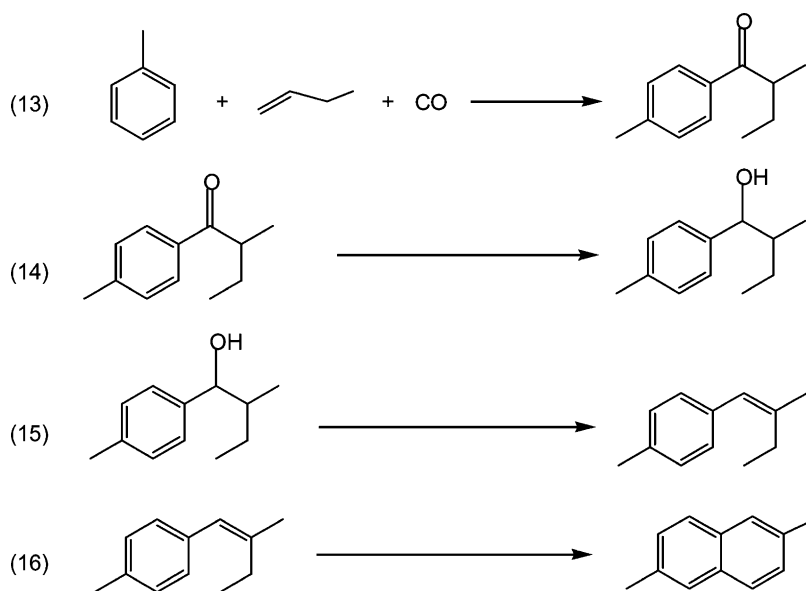

Scheme 3.
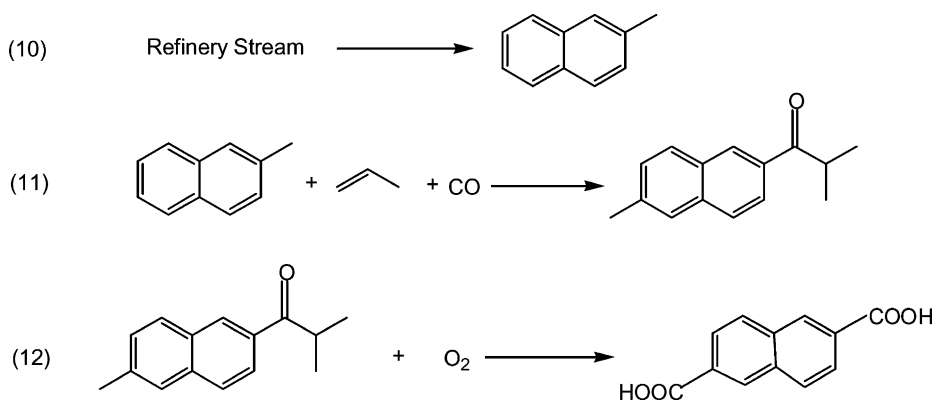
Scheme 4.

resulting from the number of process steps and the hydrogen fluoride-boron trifluoride technology, which is an environmental concern. BP Amoco determined that neither of these processes are as economically attractive as the *o*-xylene + butadiene route. MGC apparently reached the same conclusion, because their future development efforts also turned to the *o*-xylene + butadiene route, which they eventually commercialized on the development scale.

2.4. Alkyl aromatic base-catalyzed condensations

Several companies have looked at the synthetic route to 2,6-DMN shown in Scheme 7, which uses *p*-xylene and butenes (butadiene) as feedstocks.

In 1976 Mitsui reported [28,29] the preparation of 3-methyl-4-(*p*-tolyl)-butane-butene (which appears to be an isomeric intermediate of the MGC route described in Section 2.3 reactions 14 and 15) in high
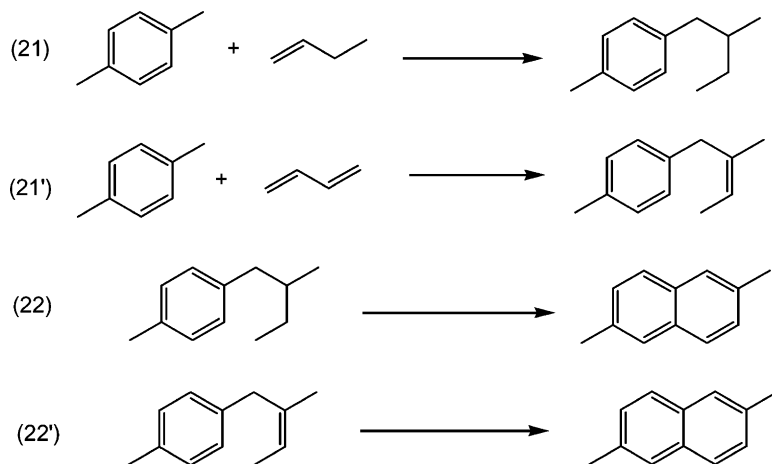

Scheme 5.
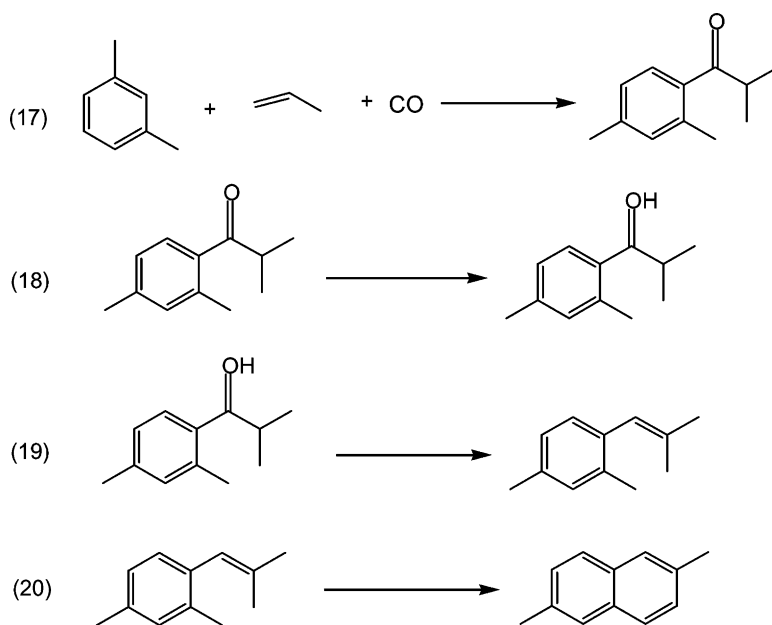
Scheme 6.

selectivity (87%) at low conversions (20–30%) using a supported sodium + potassium catalyst. The dehydrocyclization is carried out using a chromium oxide on alumina, rhenium oxide on alumina or a mixed rhenium oxide/chromium oxide catalyst system to give moderate yields (25–30%) of 2,6-DMN with the saturated sidechain intermediate (22), and good

yields (70%) with the unsaturated sidechain intermediate (22′).

In the mid 1990s a new company, Optatech Corp. (a management buy-out company stemming from Finland Neste Chemical [30]), reported improvements in this process based on newly developed catalysts [31–33]. The base-catalyzed addition of the C_4

Scheme 7.

Table 1
2,6-Dimethylnaphthalene (DMN) cost comparison[a] (US Gulf Coast, 4Q99 Basis)

Process	Cyclization (Amoco)	Cyclization (Optatech)	Alkylation (Kobe–Mobil)
Capacity (million lb per year)	75	75	75
Investments (million US$)			
ISBL	54.7	45.3	43.7
OSBL	18.3	15.2	19.1
OPC	18.3	15.1	15.7
Fixed capital	91.3	75.6	78.5
Working capital	6.9	8.1	6.3
Total capital employed	98.2	83.7	84.8
Cost of production (cents/lb)			
Raw materials[b]	31.54	64.7	34.39
By-product credits	−1.27	−10.76	−0.23
Net raw materials	30.27	53.94	34.16
Utilities	4.75	4.75	3.74
Variable costs	35.01	58.69	37.90
Fixed costs	14.37	11.96	9.41
Cash cost	49.38	70.65	47.30
Depreciation	10.95	9.07	9.20
10% ROI	13.10	11.16	11.3
Cost plus ROIC[c]	73.43	90.88	67.80[d]

[a] Chem systems PERP report 99/00S7, "2,6-dimethylnaphthalene (2,6-DMN)" (June 2000).
[b] *o*-Xylene = *p*-xylene = US$ 0.21/lb, butadiene = US$ 0.17/lb, MeOH = US$ 0.056/lb, naphthalene = US$ 0.35/lb.
[c] Not including SAR.
[d] The 2,6-DMN production economics shown in here for the Kobe–Mobil process appear to error on the low side for two reasons: (1) the raw material consumption is very optimistic and, (2) because of the large recycle streams and high pressure specialized crystallization, the capital seems very low.

feedstock to the *p*-xylene is conducted using a supported sodium or potassium catalyst. The cyclodehydration is carried out with a potassium-modified chromium oxide on alumina catalyst. See Table 1 (Section 4) for a comparison of the economics of this *p*-xylene + C₄-based process to *o*-xylene and naphthalene-based processes. It is believed that Optatech was recently engaged in pursuing this technology.

2.5. Aromatic alkylations

Several routes to 2,6-NDA and 2,6-NDC starting with the alkylation of an aromatic ring have been reported and developed by many companies over the years. The route beginning with naphthalenic compounds would appear to have an economic advantage, because reaction steps are saved not having to build the naphthalene ring.

2.5.1. Naphthalene alkylation

The routes described in this section starting with naphthalenics can be based on pure feedstocks or refinery streams containing naphthalene compounds. A 1992 Teijin patent application [34] describes a process for the two-step methylation of naphthalene shown in Scheme 8. In the first reaction, naphthalene is reacted with a DMN isomer recycle stream to produce methylnaphthalenes (MN). Simultaneously, DMN isomers are isomerized over the catalyst to increase the ratio of 2,6-DMN/2,7-DMN in the product. The second step involves the methanol methylation of the MN product from the first step to produce a 2,6-DMN-rich stream. Both reaction steps involve zeolite catalysts. However, this does not appear to be an economical process, because the reported yields for the individual reaction steps are low, and substantial recycle is involved (Scheme 8).
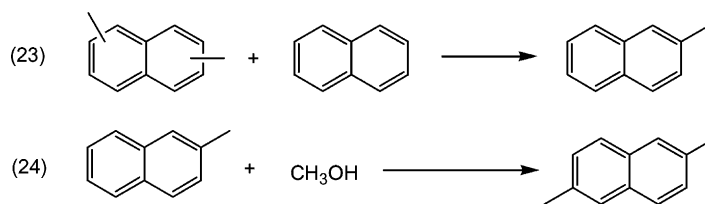
Scheme 8.

More recently, in 1996 Mobil Technology company and Kobe Steel announced that they were developing a new process that promised to lower the cost of producing 2,6-DMN. This new technology, based on the methylation of naphthalene, combined Mobil's zeolite catalyst technology and Kobe's unique purification technology. A Kobe–Mobil patent [35] described Mobil's MCM-22 large pore zeolite as the preferred catalyst for both catalytic steps in this process. Again, similar to the above Teijin process, the yields for the individual reactions are very low and appear uneconomical. Process economics comparing this naphthalene-based route to o-xylene and p-xylene-based routes is shown in Table 1 (Section 4).

Because of the higher theoretical weight percentage yield (and corresponding economic factors) resulting from the oxidation of 2,6-DMN than the higher carbon chain-substituted dialkyl naphthalenes (methyl = 138%, ethyl = 117%, isopropyl = 102%), a large research effort has gone into making 2,6-DMN as the oxidation feedstock. However, because it is easier to selectively produce the higher carbon number 2,6-dialkyl naphthalenes, many research groups have developed processes based on these materials.

Nippon Steel Co., BP Amoco and Catalytica, to name a few, have reported some success in selectively producing 2,6-DEN. Nippon Steel reported [36] a process for making 2-alkyl-6-ethylnaphthalene by the alkylation (transethylation) of a 2-alkylnaphthalene with a polyethylbenzene using a zeolite Y. The disadvantages of this process are poor selectivity to the 2,6 isomer and the need for extensive recycle.

A BP Amoco patent [37] described a transethylation process where tetraethyl benzene is used as the alkylating agent for naphthalene. The drawbacks to this process involve an aluminum chloride/red oil catalyst system, which is an environmental problem, and the production of high molecular by-products in the

many recycle streams, which are needed because of the low conversions in the individual reactions.

Catalytica has reported [38] some success using large pore zeolites such as ZSM-12, but the conversions are low and the 2,6-DEN selectivity was not high enough to be considered as an economical process.

The isopropylation of naphthalene over zeolites to produce DIPNs offers the increased opportunity to stereoselectively differentiate the desired 2,6-DIPN from 2,7-DIPN.

In addition to the Nippon Steel/Chiyoda DIPN process which was reported to be semi-commercial in 1992 [11], Catalytica has done much work in this area [39–41]. They describe a two-step process involving the isomerization of DIPNs over a silica-alumina catalyst and the selective di-isopropylation of naphthalene using H-mordenite as the shape selective zeolite.

2.5.2. Benzene alkylation

Several processes have been proposed to produce 2,6-DMN by using an acid-catalyzed alkylation of the benzene ring as the initial step in multi-step processes.

Scheme 9 shows the two-step process Mobil proposed beginning with toluene [42]. The first step involves alkylating toluene with 1-pentene over a wide range of zeolite catalysts. The isoamyltoluene formed in the first step is then dehydrocyclized in the second step using a Pt/Ba/K zeolite L, for example, to produce a DMN stream, containing some 2,6 isomer. Because these two reaction steps give low conversion and relatively low selectivity to 2,6-DMN, a recycle scheme involving an isomerization and alkylation reaction would be necessary.
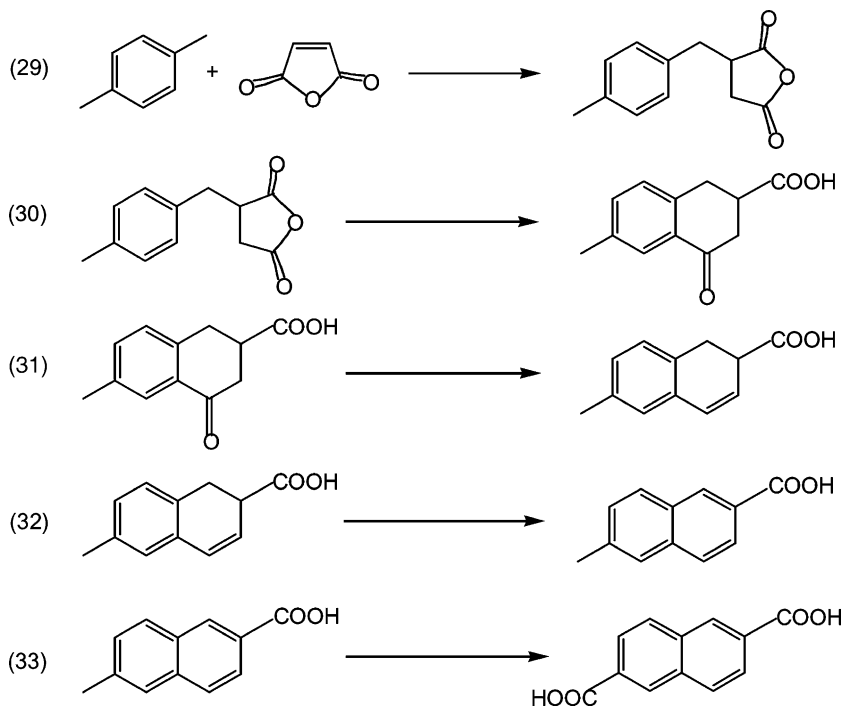
Recently, a patent issued to Chevron [43] describes a two-step process very similar to the above Mobil process but uses crude refinery streams, one rich in toluenes and the other rich in pentenes. The alkylation step is carried out using any number of acid catalysts, and the cyclodehydrogenation step uses

(25)

(26)

Scheme 9.

(27)

(28)

Scheme 10.

(29)

(30)

(31)

(32)

(33)
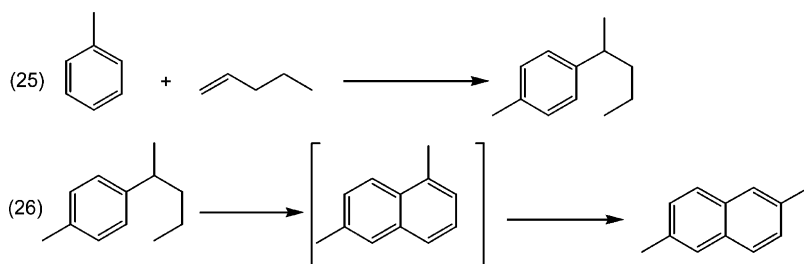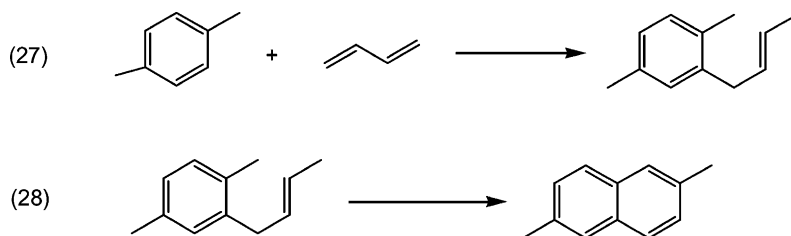
Scheme 11.

a platinum-rhenium on alumina-reforming catalyst. This process also incorporates a major recycle stream, which helps improve the overall selectivity relative to the Mobil process.

Two different processes have been reported using *p*-xylene as the alkylation feedstock in the first step. In one of the processes, Mitsubishi Petrochemical (MCC) [44] reported the two-step process shown in Scheme 10, where *p*-xylene is alkylated with butadiene over a USY zeolite in the first step to produce 2,5-dimethyl-(2-butenyl)-benzene. Both MCC and Mitsui [45] report the second step dehydrocyclization reaction taking place over a chromium oxide on alumina catalyst. The selectivity of the dehydrocyclization reaction to 2,6-DMN is in the 30–40% range.

The other *p*-xylene alkylation process is an interesting multi-step process described by MCC in a 1995 patent [46] as shown in Scheme 11. Maleic anhydride is first (29) condensed with *p*-xylene to give *p*-benzyl succinic anhydride via a free radical reaction. The second step, cyclization (30), is carried out using a strong acid catalyst to produce the tetralone derivative. In the third step (31) the keto group is hydrogenated using a precious metal catalyst, and then the tetralin intermediate is dehydrogenated (also using a precious metal catalyst) in the fourth step (32) to give the 6-methyl-2-naphthoic acid. The final oxidation step (33) to give 2,6-NDA is carried out using a MC oxidation or similar liquid phase molecular oxygen oxidation.

An interesting twist on this process has been recently reported by Cosmo Oil [47], where they condense toluene with methyl succinic anhydride to form an adduct which in a series of steps undergoes chemistry very similar to the above MCC route to give 2,6-DMN.

3. The BP Amoco 2,6-NDC process

The chemistry employed in the BP Amoco commercial 2,6-NDC process is the same as that investigated earlier by Sun–Teijin (1–6). The general process flow diagram is shown in Fig. 1c.

3.1. Alkenylation section

In the alkenylation (DMN) section (Fig. 2) *o*-xylene and butadiene are reacted using a liquid NaK (a eutectic mixture, 22% Na/78% K) strong base catalyst in a series of stirred-tank reactors. See reaction (3). BP Amoco has reported NaK catalyst system improvements by using ultrasound (sonication) to improve the NaK dispersion and increase the 5-OTP selectivity [48,49]. The 5-OTP is formed in high selectivity, but the *o*-xylene conversion is kept fairly low to avoid excessive by-product formation. The major by-products for the reaction are the various higher molecular weight isomers formed by the addition of more than one butadiene to the *o*-xylene. The product stream is quenched with water to avoid getting highly reactive NaK downstream.

The 5-OTP is cyclized to 1,5-DMT over an acidic zeolite catalyst to yield 1,5-DMT as shown in reaction (4) [50]. The reaction is high yielding, because the heavy by-products (mostly DMT–OTP dimer) can be "cracked" back to starting materials in an equilibrium type system [51–53].

Dehydrogenation of the 1,5-DMT to produce 1,5-DMN is shown in reaction (5). This elevated temperature reaction is carried out using a platinum group metal component on a alkali metal salt treated alumina support [54]. Even though this is a high yielding reaction, minor amounts of the by-products are produced, some of which are shown in Fig. 3.

The 1,5-DMN isomerization (reaction (6)) is carried out in a fixed-bed liquid phase reaction over a modified zeolite beta catalyst [55]. The isomerization is equilibrium controlled and gives a maximum of about 48% of the desired 2,6-DMN isomer at equilibrium. The DMN isomers can be divided into three groups of three (triads) and an additional single isomer for a total of 10 isomers. Fig. 4 shows these isomer groupings.

It is relatively easy to isomerize within any one of the triads shown above, but it is difficult to isomerize between triads [7]. It has been reasoned [7] that there must be a migrational barrier between the adjacent beta positions, as well as between the two rings of the naphthalene nucleus. These migrational barriers can be described in terms of the stability of the intermediate complexes shown in Fig. 4 (37 and 38). In both cases the migrations would result in the loss of the energy stabilization of the aromatic ring (Fig. 4).

The product stream from the isomerization reaction is a crude mixture of the 2,6-DMN triad isomers. This mixed isomer stream is purified by melt crystallization [56] and sent to the oxidation section.
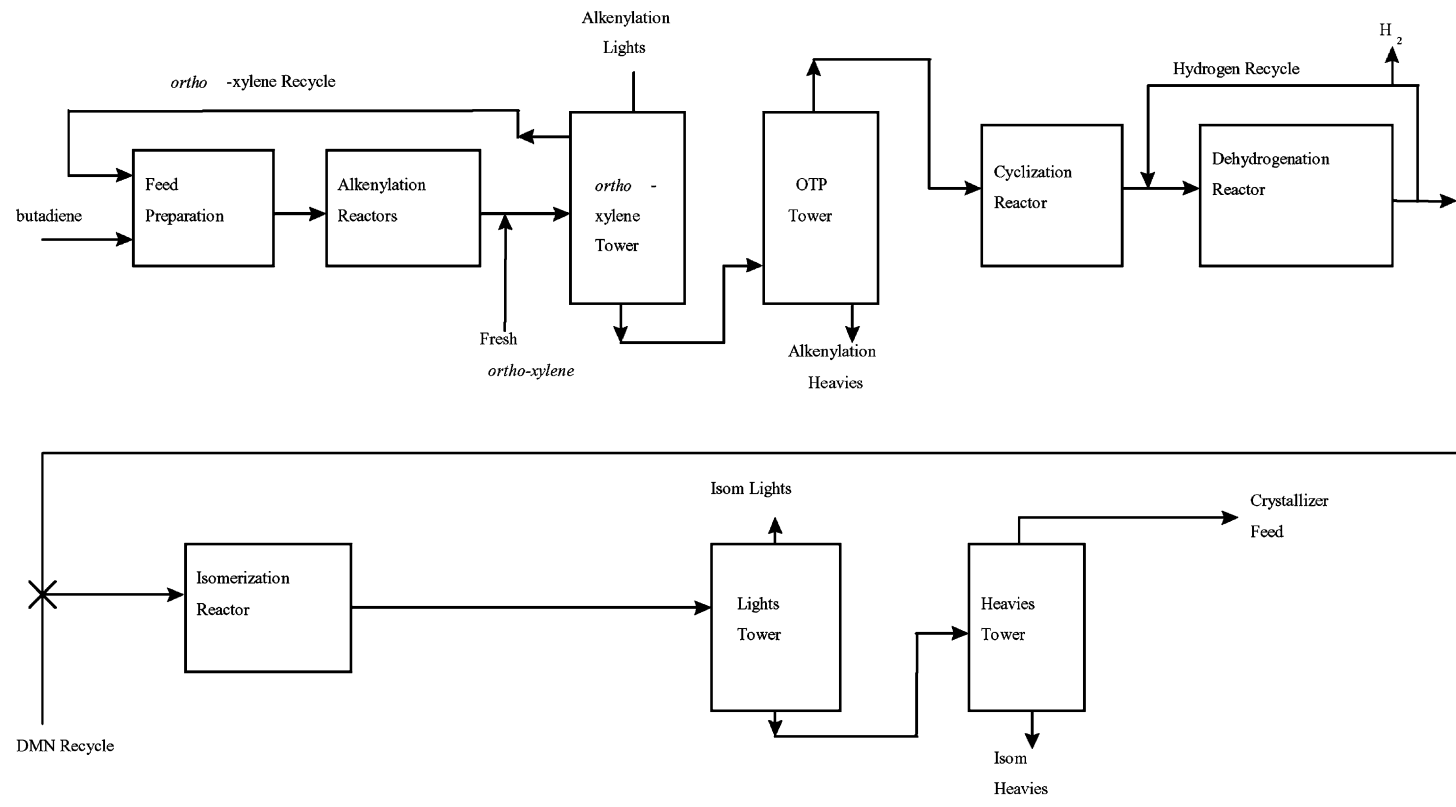
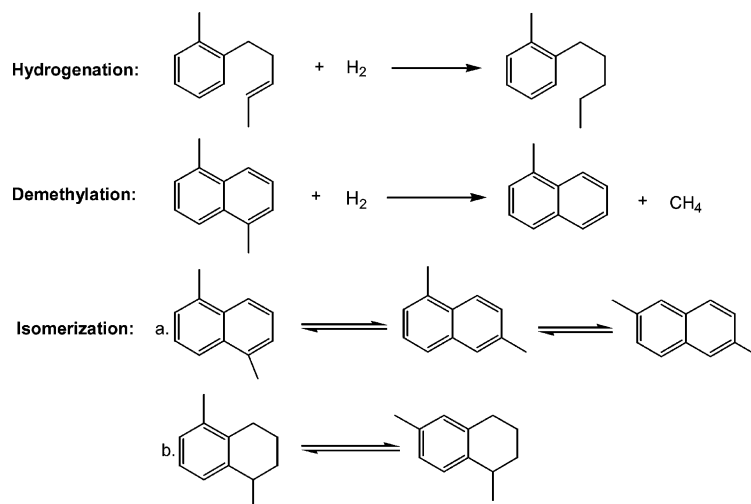Fig. 2. BP Amoco alkenylation process block diagram.

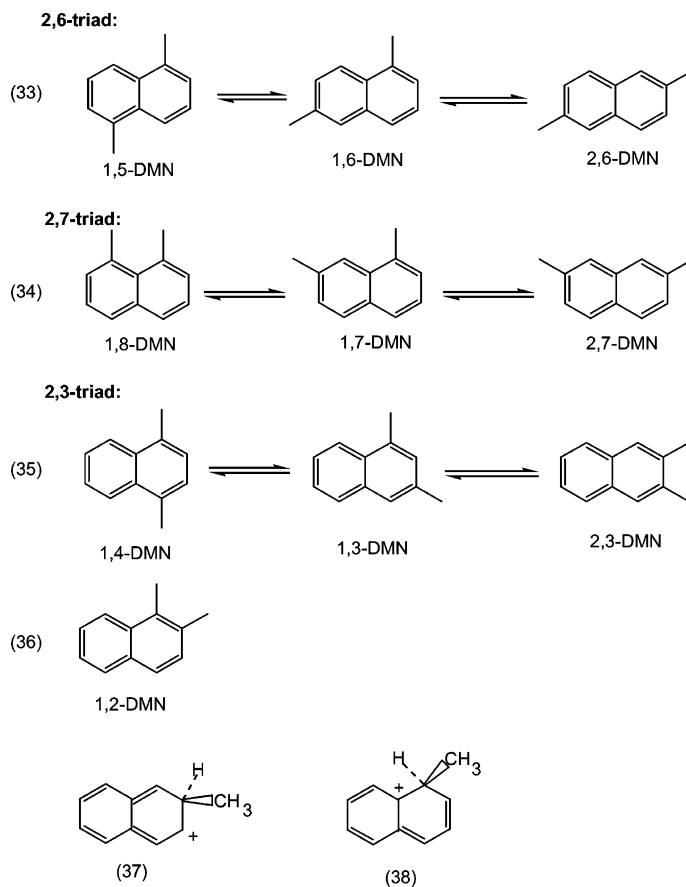Fig. 3. 1,5-Dimethyltetraling dehydrogenation by-product reactions.

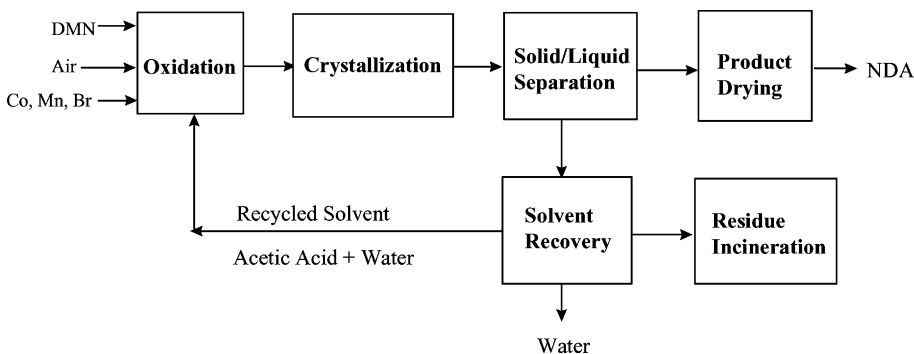Fig. 4. Scheme of dimethylnaphthalene isomers.

Fig. 5. BP Amoco 2,6-DMN oxidation process block diagram.

The economics of the BP Amoco 2,6-DMN process (*o*-xylene + butadiene) is compared to the Optatech process (*p*-xylene + C$_4$) and the Kobe–Mobil process (naphthalene + methanol) in Table 1 (Section 4).

3.2. Oxidation section

In the oxidation reaction (1), Fig. 5, the purified 2,6-DMN is reacted under MC oxidation conditions [57] to produce crude 2,6-NDA.

The crude acid is crystallized and dried. If necessary, a post-oxidation treatment step is practiced which can improve the purity of the 2,6-NDA [58] before it goes on to esterification. For polymerization processes using the di-acid (instead of the diester) a highly purified version of 2,6-NDA is necessary which requires additional processing steps. This purification of the crude 2,6-NDA to produce purified 2,6-NDA (2,6-PNDA) will be discussed in Section 4.

3.3. Esterification section

The crude 2,6-NDA is reacted in the esterification section with methanol (2), Fig. 6, to produce 2,6-NDC.
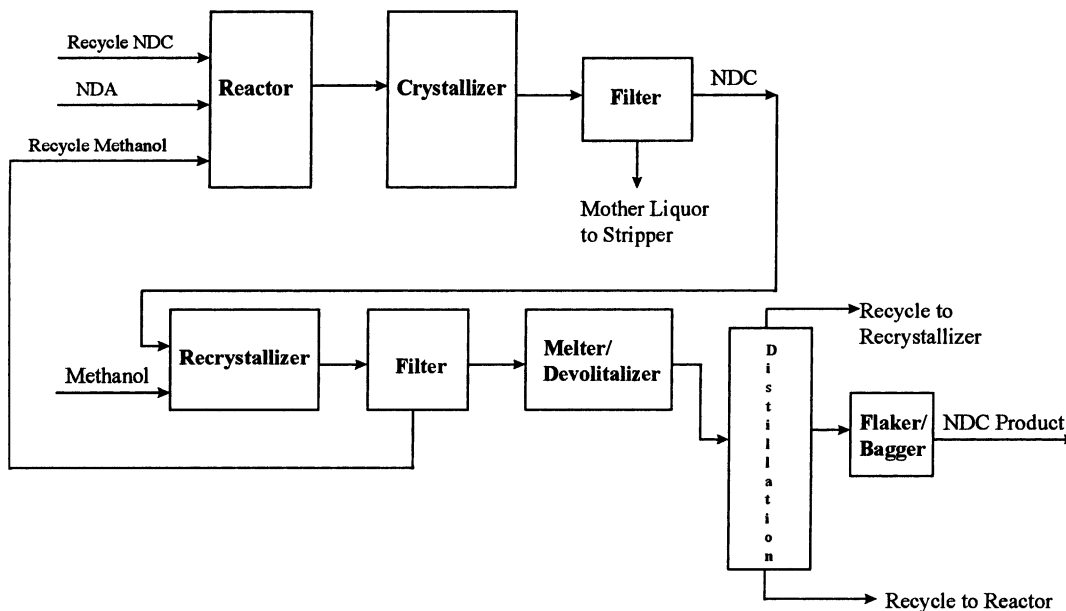

Fig. 6. BP Amoco 2,6-NDA esterification process block diagram.

The esterification is a much more difficult reaction than the esterification of a dicarboxylic acid such as terephthalic acid, because of its lower solubility in the reaction system. The continuous esterification reaction is carried out in a multi-zone reactor at high temperature and pressure [59]. The purification of the 2,6-NDC is carried out by crystallization, with additional vacuum distillation necessary for those applications requiring low levels of particulate [60].

4. Substrate economics

An economic comparison of three prominent 2,6-DMN processes which produce different substrates for the oxidation to 2,6-NDC is shown in Table 1. Each process is based on different raw material feedstocks. However, the cost of 2,6-DMN produced by the Kobil–Mobil process appears to be extremely optimistic, because raw material costs appear low, and because the capital is too low for the large recycle streams and the specialized high pressure crystallization purification (Table 1).

Table 2 shows a comparison of 2,6-NDC produced from the *o*-xylene + butadiene-based process versus 2,6-NDC produced from a methylnaphthalene-based process (probably using refinery stream methylnaphthalene) for similar sized production units.

5. Purified 2,6-NDA (2,6-PNDA)

Purification of crude 2,6-NDA is necessary if the di-acid is to be used in polymerization processes instead of the diester 2,6-NDC. Polyester made from the crude di-acid exhibits poor color and other

Table 2
Dimethyl-2,6-naphthalenedicarboxylate (NDC) production costs[a] (PEP cost index: 580)

Route	2-Methylnaphthalene	*o*-Xylene
Capacity of NDC (million lb per year)	44	50
Investment (million US$)		
ISBL	74.5	71.8
OSBL	59.2	57.4
Total fixed capital (TFC)	133.7	129.1
Production costs (cents/lb)		
Raw materials	151.37	43.28
Utilities	14.04	9.39
Variable costs	165.41	52.67
Operating labor, 8 per shift, US$ 28.75/h	4.58	6.04
Maintenance labor, 1.6% per year of ISBL	2.71	2.30
Control lab labor, 20% of operating labor	0.92	1.21
Labor costs	8.21	9.55
Maintenance materials, 2.4% per year of ISBL	4.06	3.44
Operating supplies, 10% of operating labor	0.46	0.60
Total direct costs	178.14	66.26
Plant overhead, 80% of labor costs	6.57	7.64
Taxes and insurance, 2% per year of TFC	6.08	5.16
Plant cash costs	190.79	79.06
Depreciation, 10% per year of TFC	30.39	25.82
Plant gate costs	221.18	104.88
G&A, sales, research	33.02	18.83
Net production cost	254.20	123.71
ROI before taxes, 25% per year of TFC	75.97	64.56
Product value	330.17	188.27

[a] SRI PEP report no. 202A, "polyethylene naphthalate monomers" (March 1997).
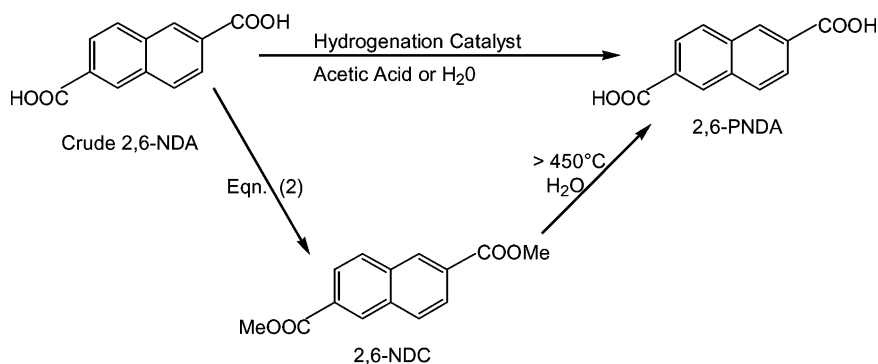
Scheme 12.

inferior properties. BP Amoco has explored two separate processes to accomplish this purification as shown in Scheme 12. The most direct route [61] is a process very similar to the purification of terephthalic acid (TA) to purified TA (PTA). This process involves hydrogenation of the crude 2,6-NDA with a noble metal hydrogenation catalyst in the presence of acetic acid or water. In addition to purity, a bonus provided by this extra processing step is the increase in particle size of the product and a reduction of "fines". The other route is through the diester (2,6-NDC) via an equilibrium reaction in an aqueous media at high temperature [62] to produce a hydrolyzed 2,6-NDA (2,6-HNDA). Since 2,6-PNDA is minimally soluble in water, the di-acid produced in this process precipitates immediately from the reaction medium in the form of fine particles (Scheme 12).

In 1996 BP Amoco technology was used in starting up a multi-million pound semi-works facility capable of producing 2,6-PNDA for acid-based polymer processes and applications. This facility is also is capable of hydrolyzing 2,6-NDC to 2,6-HNDA having purity levels greater than 99.9%.

6. Physical properties

The physical properties of 2,6-NDA, 2,6-NDC, 2,6-DMN and its intermediates are given in Table 3.

5-OTP and 1,5-DMT are clear, colorless liquids with fairly high boiling points. 5-OTP has a strong, penetrating odor. The two DMNs (1,5-DMN and 2,6-DMN), 2,6-NDA and 2,6-NDC are white, crystalline solids at ambient conditions.

7. Naphthalate polymer applications

It is interesting to note that the starting point for PEN and other naphthalate polymers is based on the low cost, readily available starting materials *o*-xylene and butadiene as shown in Scheme 13.
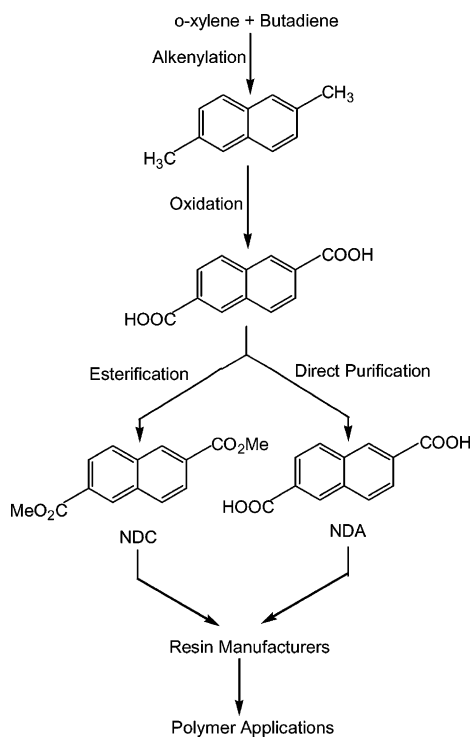

Scheme 13.

Table 3
Physical properties

Physical property	5-OTP-2	1,5-DMT	1,5-DMN	2,6-DMN	NDA	NDC
Molecular weight	160	160	156	156	216	244
Appearance	Clear colorless liquid	Clear colorless liquid	White solid	White solid	Tan to white powder	White powder
Density 15 °C (g/cm^3)	0.90	0.96	Solid	0.91 at 125 °C	0.3–0.7 (bulk) 1.4–1.5 (intrinsic)	0.61–0.68 (bulk) 1.4–1.5 (intrinsic) 1.10 at 200 °C 1.03 at 260 °C
Density by displacement (g/cm^3)	–	–	1.11	1.07	–	–
Flash point (°C)	71	98	114	101	>232	>232
Kinematic viscosity						
40 °C (cSt)	1.48	–	–	Solid	Solid	1.07 (cSt) at 195 °C
50 °C (cSt)						0.967 (cSt) at 205 °C
100 °C (cSt)	0.84	–	–	Solid	Solid	0.855 (cSt) at 219 °C
Freezing point (°C)	−84	<−62	82	112	–	–
Boiling point (°C)	227	240	265	262	–	–
API gravity at 60°F	26.18	15.45	Solid	Solid	Solid	Solid
Manual pour point (°C)	<−63	<−60	Solid	Solid	Solid	Solid
Melting point (°C)	Liquid	Liquid	82	110	>300 Decomposes before melting	190
Solubility in water	–	–	–	–	Negligible, below 0.1%	Negligible below 0.1%
Autoignition temperature (°C)	–	–	–	–	500 (dust cloud in air) 375 (dust layer in air)	398 (dust cloud in air) 190 (dust layer in air)

7.1. PEN applications

7.1.1. Films

2,6-NDC and 2,6-NDA are specialty polymer intermediates that can be used to manufacture polyester resins for high performance polymers. When reacted with ethylene glycol, the homopolymer produced is PEN. 2,6-NDA and 2,6-NDC-based polyesters derive their performance improvements from the double ring structure of the naphthalene molecule. This double ring structure in the polyester chain boosts thermal, mechanical and barrier performance versus polyester polymers based on the terephthalate or benzene molecule. The star in Fig. 7 compares the properties of PEN with the terephthalate-based polyester polyethylene terephthalate (PET).

In the film area, PEN effectively fills the gap in modulus and continuous use temperature which exists between PET and the very high performance polyimide films and polyaramide films. The thermal, mechanical, electrical and barrier properties of PEN as well as its heat, chemical, hydrolytic and radiation resistance are superior to that of PET. The thermal and mechanical properties of biaxially-oriented PEN film can be varied depending upon the stretching and heat set conditions used during film production to meet the needs of a wide variety of potential end use environments.

The enhanced property performance of naphthalate resins allows the packaging engineer greater design freedom and extends the current use for polyesters to more demanding applications. Table 4 lists some of the
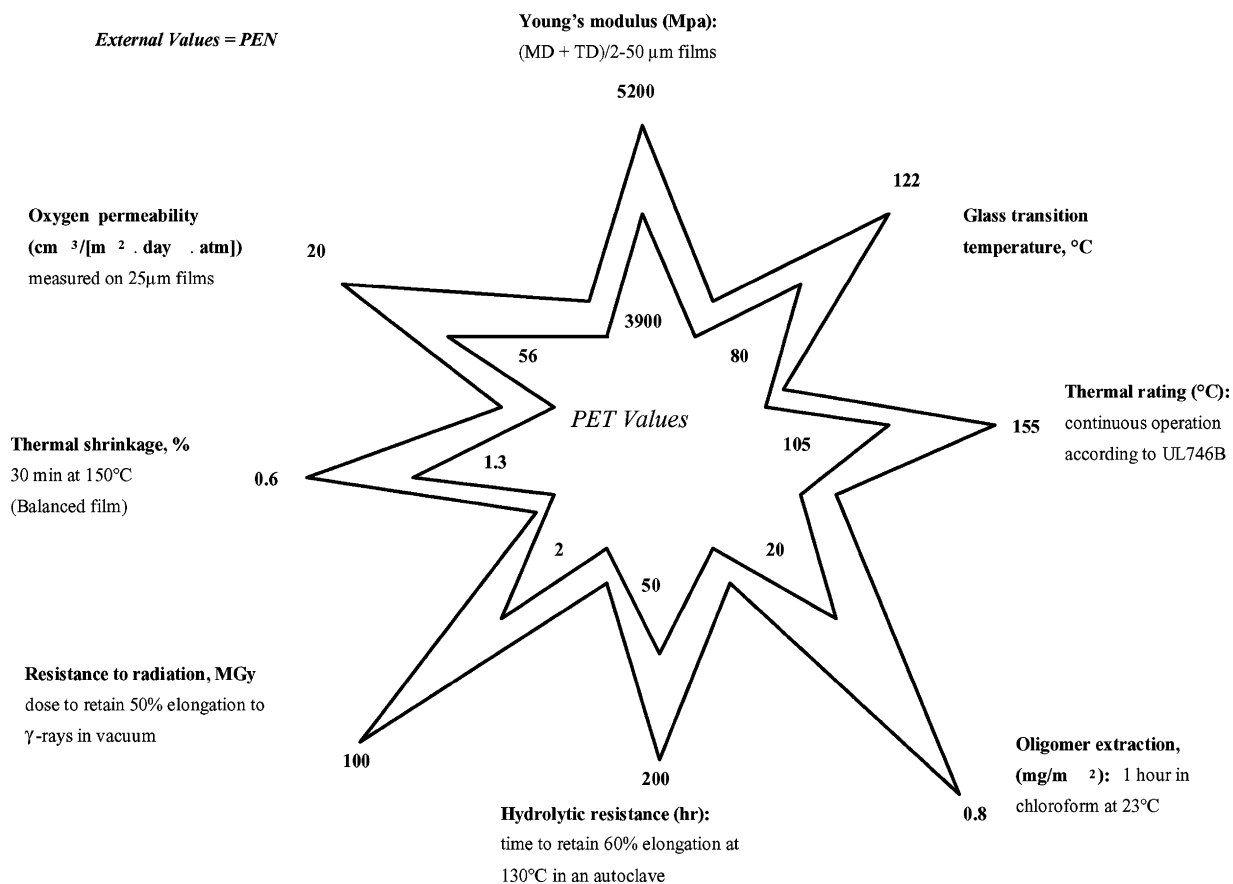

Fig. 7. Comparative properties of PEN vs. PET film [63].

Table 4
Packaging applications

Application	NDC benefit	Resin type
Small-sized carbonated beverage bottle (<0.5l)	Improved barrier	Copolymers
	Extended shelf life	Blends
Returnable/refillable	Improved thermal resistance (washing)	Copolymers
Mineral water	Improved chemical resistance (washing)	Blends
Juice	Reduced flavor carryover	PEN
Beer	Reduced adsorption	PEN
Soft drinks	Reduced adsorption	PEN
Pasteurized milk	Reduced adsorption	PEN
Beer	Improved barrier	PEN
Hot-fill applications	Improved thermal resistance	PEN
Foods	Improved barrier	Copolymers
Beverages	Improved barrier	Blends
Baby food (retort)	Improved thermal resistance	PEN
Pharmaceutical/cosmetic	Barrier	PEN
	Chemical resistance	Copolymers
	UV resistance	Blends
Industrial	Barrier	PEN
	Chemical resistance	Copolymers
	Chemical resistance	Blends

packaging applications where naphthalate polymers find use.

7.1.2. Fibers

When PEN is spun into fibers, a key reason it improves PET performance is its greater structural stability at the molecular level. This translates into higher modulus, tenacity, and resistance to stretching and shrinkage. Because it takes more energy to destabilize its molecule, PEN also has greater resistance to thermal and chemical attack. The margin of improvement is even greater when comparing PEN fiber with nylon or rayon, as seen in Table 5.

The automobile industry is expected to offer a significant opportunity for PEN fibers in tire cord and under-the-hood uses such as hoses and belts. PEN tire cord has found use in both the tire carcass and tire belts. The fiber's high modulus and resilience will yield better handling for easier and faster turning. Road noise reduction has been found to be a significant feature of PEN tires, but the biggest benefit of all to car owners may be longer tire life. A lighter, more resilient and heat-resistant tire should last longer. Non-tire automotive uses for PEN fibers such as radiator hoses and V-belts, often involve harsh environments such as dynamic stresses and exposure to heat, water, and corrosive chemicals that PEN can protect against.

7.1.3. PEN versus PET film economics

Table 6 shows the cost of production of PEN and PET films. The product value of the PEN would be

Table 5
PEN outperforms PET, nylon and rayon

Fiber property	PEN	PET	Nylon 6/6	Rayon
Tenacity (g/denier)	10	9	9	5
Modulus (g/denier)	350	110	50	125
Shrinkage in boiling water (%)	1	5	8	Decomposes

Table 6
Polyester film production costs[a] (PEP cost index: 550)

Product	PET	PEN
Capacity (million lb per year)	33	33
Investment (million US$)		
ISBL	76.1	75.9
OSBL	24.1	24.1
Total fixed capital (TFC)	100.2	100.0
Production costs (cents/lb)		
Raw materials	52.00	380.09[b]
Utilities	5.55	6.39
Variable costs	57.55	386.48
Operating labor, 6 per shift, US$ 24.68/h	5.24	5.24
Maintenance labor, 1.6% per year of ISBL	3.69	3.68
Control lab labor, 20% of operating labor	1.05	1.05
Labor costs	9.98	9.97
Maintenance materials, 2.4% per year of ISBL	5.53	5.52
Operating supplies, 10% of operating labor	0.52	0.52
Total direct costs	73.58	402.49
Plant overhead, 80% of labor costs	7.98	7.98
Taxes and insurance, 2% per year of TFC	6.07	6.06
Depreciation, 10% per year of TFC	30.36	30.30
Plant gate costs	117.99	446.83
G&A, sales, research	10.21	27.50
Production cost	128.20	474.33
ROI before taxes, 25% per year of TFC	75.91	75.76
Product value	204.11	550.09

[a] SRI PEP report no. 159B, "specialty plastics film" (August 1993).

[b] 2,6-NDC raw material cost was assumed to be US$ 3.15/lb instead of the current BP Amoco price of US$ 2.50/lb for film applications.

lowered to under US$ 5/lb if the current BP Amoco price of US$ 2.50/lb for 2,6-NDC were used instead of SRI's assumed price of US$ 3.15/lb. It is also very likely that the cost of PEN will be lowered to <2PET's cost when 2,6-NDC and PEN capacities increase.

7.2. Engineering polymer applications

2,6-NDC and 2,6-NDA are also finding use in the area of thermoplastic polyester engineering polymers. Polybutylene naphthalate (PBN) is the homopolymer of 2,6-NDC and butanediol. Used as a molding resin, some of the end-uses are as connectors, switches and other electronic packaging devices where its high heat deflection temperature, chemical resistance, thermal aging, elongation, and dimensional stability meet the demanding requirement of the electronics industry. In the automotive market PBN's excellent vapor barrier properties hold potential for application in fuel-related parts such as hoses, lines and tanks.

Amorphous PEN (A-PEN) with its clarity, heat and chemical resistance, and barrier properties exhibits increased performance in injection molded, extruded sheet and thermoformed applications.

In the area of thermoplastic elastomers (TPEs) PBN-based copolyester ether elastomers exhibit excellent split tear strength. Elastomers with PBN and PEN-modified hard segments exhibit increased heat, chemical and hydrolysis resistance.

Thermotropic liquid crystalline polymers (LPCs) based on 2,6-NDA exhibit outstanding flow and molding residence time (a key in small part electronic device fabrication), high-temperature performance, excellent dimensional stability and chemical

resistance, inherent flame-retardance and outstanding dielectrics.

Acknowledgements

References

[1] R. Barker, A. Saffer, US 2,833,816 (1955) to Mid-Century Corp.

[2] J. Allen, E. Malmberg, US 3,235,615 (15 February 1966) to Sun Oil.

[3] R. Barbor, E. Malmberg, US 3,565,945 (23 February 1971) to Sun Oil.

[4] K. Ogata, K. Shimosato US 3,671,578 (20 June 1972) to Teijin Ltd.

[5] G. Eberhardt, US 3,244,758 (5 April 1966) to Sun Oil.

[6] G.C. Eberhardt, H.J. Peterson, J. Org. Chem. 30 (1965) 82.

[7] G. Suld, A.P. Stuart, J. Org. Chem. 29 (1964) 2939.

[8] T. Harad, S. Kurozumi, S. Nagahama, T. Nishikawa, K. Shimada, Y. Takeuchi, US 3,798,280 (19 March 1974) to Teijin Ltd.

[9] M. Ogasawara, I. Oka, T. Shima, T. Urasaki, US 3,851,002 (26 November 1974) to Teijin Ltd.

[10] K. Yamamoto, G. Yamashita, US 3,870,754 (11 March 1975) to Teijin Ltd.

[11] Chem Systems' PERP report, 2,6-Naphthalene Dicarboxylic Acid, January 1991.

[12] Chemical Week, February 1992, p. 22.

[13] Japan Chemical Week, 2 May 1996, p. 2.

[14] M. Rule, G.C. Tustin, US 4,795,737 (5 January 1989) to Eastman Kodak.

[15] G.C. Tustin, M. Rule, J. Catal. 147 (1994) 186–198.

[16] G.R. Stienmetz, M. Rule, US 4,845,273 (4 July 1989) to Eastman Kodak.

[17] G.R. Steinmetz, M. Rule, V.H. Agreda, L.C. Treece, US 4,778,918 (18 October 1988) to Eastman Kodak.

[18] S. Mitamura, Y. Kata, K. Fujishiro, Y. Tsutsumi, US 5,081,252 (1992) to Nippon Steel.

[19] S. Fujiyama, S. Matsumoto, T. Yanagawa, EP 215,351 (25 March 1987) to MGC.

[20] Chemistry and Industry (Japan) Vol. 43, No. 3 (1990), pp. 96–98.

[21] S. Fujiyama, S. Matsumoto, T. YanaGawa, JP 060188343 (25 September 1985) to MGC.

[22] T. Takefumi, T. Abe, JP 063,115,843 (20 May 1988) to MGC.

[23] T. Takefumi, Y. Shiokawa, S. Matsumoto, N. Tokura, EP 517,979 (16 December 1992) to MGC.

[24] T. Tanaka, M. Inri, US 4,886,902 (12 December 1989) to MGC.

[25] N. Tokura, T. Takefume, T. Yanagawa, Y. Shiokawa, I. Ohtsuka, EP 361,479 (28 September 1989) to MGC.

[26] T. Abe, S. Uchiyama, T. Ojima, K. Kida, US 5,008,479 (16 April 1991) to MGC.

[27] T. Abe, S. Ebata, H. Machida, K. Kida, US 5,023,390 (11 June 1991) to MGC.

[28] K. Taniguchi, S. Miyamoto, H. Matsuoka, US 3,931,348 (6 January 1976) to Mitsui.

[29] H. Matsuoka, S. Miyamoto, K. Taniguchi, US 3,931,348 (6 January 1976) to Mitsui.

[30] European Plastics News, June 1997, p. 38.

[31] K. Vahteristo, E. Halme, S. Koskimies, S. Csicsery, M. Laatikainen, V. Niemi, WO 97/02225 (23 January 1997) to Optatech.

[32] I. Kiricsi, S. Koskimies, S. Csicsery, WO 97/24305 (10 July 1997) to Optatech.

[33] J. Jakkula, V. Niemi, K. Vahteristo, K. Sahala, WO 97/30012 (21 August 1997) to Optatech.

[34] K. Sumitani, K. Shimada, JP 0413637 (17 January 1992) to Teijin Ltd.

[35] M. Motoyuki, K. Yamamoto, J. McWilliams, R. Bundens, US 5,744,670 (28 April 1998) to Kobe–Mobil.

[36] G. Takeuchi, M. Shiroshita, K. Kariu, Y. Shimoura, WO 92/02473 (20 February 1992) to Nippon Steel.

[37] G. Hagen, T. Nemo, US 4,873,386 (10 October 1989) to BP Amoco.

[38] J. Fellmann, P. Massiani, H. Exner, P. Wentrcek, R. Saxton, WO 91/05751 (2 May 1991) to Catalytica.

[39] S. Newman, J. Fellmann, P. Kilner, US 5,003,120 (26 March 1991) to Catalytica.

[40] J. Fellmann, R. Saxton, P. Wentrcek, E. Derouane, US 5,003,122 (26 March 1991) to Catalytica.

[41] J. Fellmann, R. Saxton, P. Wentrcek, E. Derouane, P. Massiani, US 5,026,942 (25 June 1991) to Catalytica.

[42] K. Del Rossi, L. Green, A. Huss Jr., G. Kirker, M. Landis, US 5,043,501 (27 August 1991) to Mobil.

[43] C. Chen, W. Schinski, D. O'Rear, T. Harris, US 5,955,641 (21 September 1999) to Chevron.

[44] T. Iwakura, N. Nishiyama, JP 6336447 (6 December 1994) to MCC.

[45] N. Sakamoto, K. Shimamoto, T. Fujimoto, K. Taniguchi, JP 1301629 (5 December 1989) to Mitsui.

[46] H. Iwane, K. Kujira, N. Suzuki, JP 7025818 (27 January 1995) to MCC.

[47] H. Takeya, H. Otsuka, JP 09143104 (3 June 1997) to Cosmo Oil.

[48] L. Lillwitz, A. Karachewski, US 5,198,594 (30 March 1993) to BP Amoco.
[49] L. Lillwitz, A. Karachewski, US 5,334,796 (2 August 1994) to BP Amoco.
[50] P. Sanchez, D. Young, G. Kuhlmann, W. Partenheimer, W. Schammel, US 4,950,825 (21 August 1990) to BP Amoco.
[51] D. Sikkenga, I. Zaenger, G. Williams, US 5,030,781 (9 July 1991) to BP Amoco.
[52] D. Sikkenga, G. Williams, I. Zaenger, US 5,034,561 (23 July 1991) to BP Amoco.
[53] D. Sikkenga, I. Zaenger, G. Williams, US 5,284,987 (8 February 1994) to BP Amoco.
[54] J. Amelse, US 5,189,234 (23 February 1993) to BP Amoco.
[55] D. Sikkenga, I. Zaenger, G. Williams, US 4,962,260 (9 October 1990) to BP Amoco.
[56] T. Smith, J. Weis, Y. Viswanath, US 5,510,563 (23 April 1996) to BP Amoco.
[57] J. Harper, G. Kuhlmann, K. Larson, R. McMahon, P. Sanchez, US 5,183,933 (2 February 1993) to BP Amoco.
[58] D. Sikkenga, G. Kuhlmann, P. Behrens, M. Zeitlin, S. Hoover, US 5,292,934 (8 March 1994) to BP Amoco.
[59] P. Behrens, J. Holzhauer, G. Hussmann, D. Sikkenga, US 5,350,874 (27 September 1994) to BP Amoco.
[60] J. Holzhauer, D. Young, M. Zeitlin, P. Behrens, US 5,262,560 (16 November 1993) to BP Amoco.
[61] D. Sikkenga, S. Hoover, US 5,256,817 (26 October 1993) to BP Amoco.
[62] J. Holzhauer, R. Albertins, S. Hoover, D. Sikkenga, US 5,563,294 (8 October 1996) to BP Amoco.
[63] Taken from DuPont Films PEN Film Brochure.